

Electrophotoluminescence of Zinc Sulfide Phosphors

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Various effects of electric fields on the light emission of zinc sulfide phosphors during or after excitation by ultraviolet or X-rays have been investigated by a number of authors¹⁻⁴. The effects include a quenching or an enhancement of the luminescence under the electric field, a momentary stimulation of luminescence at application or removal of the electric field, and other miscellaneous effects.

If the observations on various phosphors, each having different kinds of activators or different chemical compositions of matrix, for example, hex.-ZnS:Cu, cub.-ZnS:Mn, (Zn, Cd)S:Ag and ZnS:Cu, Pb are carried out under the same conditions, then each phosphor has different influences. The purpose of this paper is to find how the influence of an alternating electric field on luminescence varies with the kinds of activator or chemical composition of the matrix.

Destriau² made extensive investigations of these effects, and he reported that it seems that the sulfides with a persistent phosphorescence are very sensitive to momentary stimulation and insensitive to the quenching effect, while the sulfides with brief phosphorescence show an appreciable quenching effect and a slight or even insignificant momentary stimulation. However, he⁵ noted that although thermoluminescence and infrared stimulation can occur after the action of the field, application of the field after thermoluminescence or infrared stimulation, on the other hand, does not produce any emission. From this observation, it might be concluded that the electric field acts only on shallow traps but not on deep traps, but he thought that this conclusion is uncertain, because the field obviously has a

directional character, whereas temperature or infrared radiation has not.

Matossi⁴ has studied the electrophotoluminescence of various zinc sulfide phosphors, but he could not find any systematic dependence of the characteristics of stimulation or quenching on the method of preparation (kind of activator or flux) or on other luminescence properties, such as the time of afterglow.

It is explained by several authors that the momentary field stimulation might be caused by electron traps, from which the electron is released by electric field and returns to luminescent centers to cause emission. Further, phosphorescence, infrared stimulation and thermoluminescence are explained by the action of electron traps. Therefore it is expected that there might be a close relation between momentary stimulation and those characteristics. From this standpoint, we are going to discuss the relations between momentary field stimulation and phosphorescence, infrared stimulation, or thermoluminescence, respectively.

Experimental

The phosphors were synthesized from the pure zinc sulfide by adding appropriate aqueous solution of activator and two weight percent sodium chloride. The mixtures were stirred well, dried, transferred to a silica crucible and fired for crystallization from 750 to 1200°C in a temperature-controlled furnace in air for half an hour. After crystallization, the preparations were washed free of water-soluble chloride and were dried. The composition of phosphors and the condition of firing are shown in columns 2 and 3 of Table I.

All phosphors were embedded in Acrylite (Polymethylmethacrylate, produced by Mitsubishi Rayon Co.) and investigated in cells of the common construction of the electroluminescent cell with about 10 cm² area and about 0.5 mm. thickness of the layer. The phosphor-dielectrics layer was held between two electrodes, one of which was conductive glass coated with tin oxide layer, and the other was aluminum

1) G. Destriau, *Phil. Mag.*, **38**, 784 (1947).

2) G. Destriau, *ibid.*, **38**, 880 (1947).

3) I. T. Steinberger, W. Low and E. Alexander, *Phys. Rev.*, **99**, 1219 (1955).

4) F. Matossi, *J. Electrochem. Soc.*, **103**, 122 (1956).

5) G. Destriau and H. F. Ivey, *Proceeding of the IRE*, **43**, 1911 (1955).

TABLE I. THE COMPOSITION OF PHOSPHORS AND THEIR LUMINESCENT CHARACTERISTICS

No.	Composition	Firing temp. °C concn. of act. mol./1 mol. ZnS		P. L.	Phospho.	I. R. S.	M. F. S.	F. Q.	Notes
1	ZnS : Ag	1000	10 ⁻⁵	b	S			+	
2	"	1150	10 ⁻⁵	"	"			+	
3	"	"	10 ⁻⁴	"	"			+	
4	"	"	10 ⁻³	"	"			+	
5	(Zn _{0.80} , Cd _{0.20})S : Ag	950	10 ⁻⁴	g	"			+	
6	(Zn _{0.50} , Cd _{0.50})S : Ag	"	"	y	"			+	
7	(Zn _{0.20} , Cd _{0.80})S : Ag	"	"	r	"			-	
8	(Zn _{0.63} , Cd _{0.37})S : Ag	1150	10 ⁻⁵	g	L		+	+	
9	"	"	10 ⁻⁴	"	"		+	+	
10	"	"	10 ⁻³	"	S			+	
11	(Zn, Cd)S : Ag	—	—	y	"			+	(a)
12	ZnS : Zn	900	—	b	"			+	
13	ZnS : Cu	"	10 ⁻⁶	g, b.	"		+	+	
14	"	"	3×10 ⁻⁶	g	"		+	+	
15	"	"	10 ⁻⁵	"	M		+	+	
16	"	"	3×10 ⁻⁵	"	"		+	+	
17	"	"	10 ⁻⁴	"	"		+	+	
18	"	"	3×10 ⁻⁴	"	S			+	
19	"	"	10 ⁻³	"	"			+	
20	"	1000	10 ⁻⁵	"	M		+	+	(b)
21	"	"	10 ⁻⁴	"	S		+	+	(")
22	"	"	10 ⁻³	"	"			+	(")
23	"	1200	3×10 ⁻⁶	"	L			+	
24	"	"	10 ⁻⁵	"	V. L	+	+	-	
25	"	"	3×10 ⁻⁵	"	"	+	+	-	
26	"	"	10 ⁻⁴	"	L			+	
27	"	"	3×10 ⁻⁴	"	"			+	
28	"	"	10 ⁻³	"	S			+	
29	"	—	—	"	V. L			-	(c)
30	(Zn _{0.80} , Cd _{0.20})S : Cu	1050	10 ⁻⁴	y	L			+	
31	(Zn _{0.50} , Cd _{0.50})S : Cu	"	"	r	S			-	
32	Zn(S, Se) : Cu	780	10 ⁻⁴	y	"			+	
33	ZnS : Cu, Fe	1200		g	"			+	
34	ZnS : Cu, Pb	1150		"	L	+		-	(d)
35	"	—	—	"	M		+	-	(e)
36	ZnS : Pb	900	—	"	"	+	+	+	
37	"	1200	—	"	L	+		-	
38	ZnS : Pb, Mn	1150		y	"	+		-	
39	ZnS : Mn	1000	10 ⁻²	o	S	+		-	
40	"	"	"	"	"		+	-	(f)
41	"	1200	"	"	"	+		-	
42	ZnS, ZnO : Mn	1000	"	"	"		+	-	
43	(Zn _{0.50} , Cd _{0.20})S : Mn	"	"	"	"	+		+	
44	"	"	"	"	"			+	(f)

(a) A commercial product for X-ray.

(b) Fired in nitrogen stream.

(c) A commercial product for phosphorescent paint.

(d) Fonda's phosphor.

(e) Electroluminescent phosphor.

(f) No flux.

TABLE I (continued)

P. L. :	Color of photoluminescence b=blue, g=green, y=yellow, r=red, g. b=greenish blue, o=orange.
Phospho. :	Phosphorescence S=short persistence, M=medium, L=long, V. L=very long.
I. R. S. :	Infrared stimulation +=weak i.r.s., ++=strong i.r.s.
M. F. S. :	Momentary field stimulation (the Gudden-Pohl effect) +=considerable m.f.s., ++=strong m.f.s.
F. Q. :	Quenching of luminescence by electric field application during excitation --=none or slight, +=considerable field quenching.

plate. A d-c operated black light lamp with a Corning glass filter 5840 transmitting from 3100 to 4200 Å served as the exciting ultraviolet source. The light emitted by phosphor was allowed to fall upon the cathode of the 1P21 photomultiplier, the anode current from the photomultiplier being measured by means of d-c amplifier and cathode ray oscillograph, and the oscillogram of transient phenomenon for emission at electric field application or removal was observed.

The applied electric field was obtained from 50 c. p. s a-c line, and field intensity was estimated to be about 10000 volts per centimeter. With this field intensity electroluminescence was not detected with the exception of zinc sulfide phosphors which contain 10^{-3} mol. or more of copper per 1 mol. ZnS.

Experimental Results and Discussion

On application of the alternating electric field during continuous ultraviolet excitation, the average brightness of luminescence increases for a moment. After these transitory phenomena the average brightness reaches a new equilibrium level, lower than the luminescent level before application of the field. Some

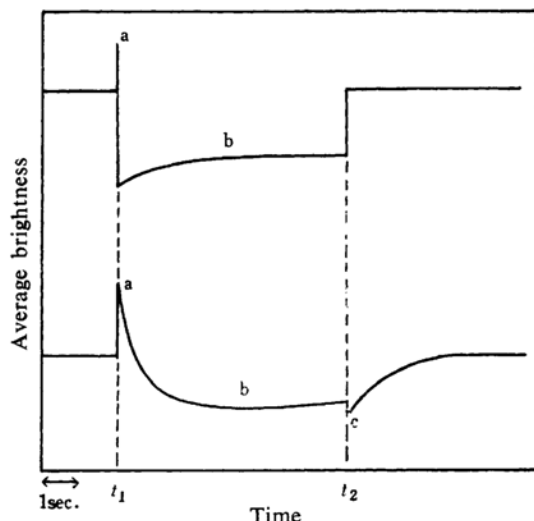


Fig. 1. Average brightness of luminescence when electric field is applied or removed. t_1 ...field application, t_2 ...field removal, a...momentary stimulation, b...field quenching, c...cut-off dip.

phosphors show no steady state quenching. The transient variation of emission is shown schematically as a function of time in Fig. 1. The field quenching lasts as long as the field is applied, and recovers gradually, then reaches a steady level.

The stimulated and quenched brightness were modulated by applied alternating electric field. A frequency of brightness wave was that of applied alternating field or twice this frequency. The modulated frequency for pure zinc sulfide phosphors was 100 c.p.s., while that of zinc-cadmium sulfide phosphors which contained 20 mol. percent cadmium sulfide or more was 50 c.p.s.. Fig. 2 shows the oscillogram of modulated wave for ZnS and (Zn, Cd)S phosphors. The (Zn, Cd)S phosphors which contain below 20 mol. percent cadmium sulfide was not studied.

When the electric field was removed, then the phosphors such as ZnS:Cu, Fe, (Zn, Cd)S:Ag (No. 11), and Zn(S, Se):Cu (No. 32) had a short flash, while the phosphors such as ZnS:Cu and (Zn, Cd)S:Cu had a dip of brightness. On the other hand, the phosphors such as the many ZnS:Ag and (Zn, Cd)S:Ag phosphors recovered directly without flash or dip. The cut-off stimulation was found by Matossi for almost all phosphors to consist of two components, a very sharp peak and a tail of long duration. We found this cut-off

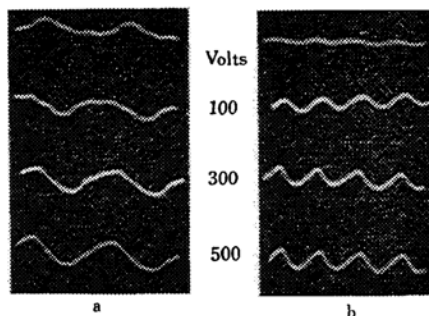


Fig. 2. Oscillogram of quenching brightness wave during 1/25 second at various voltage. The patterns of 'a' show quenching brightness waves of (Zn, Cd)S:Ag, and they are modulated to 50 c.p.s. The patterns of 'b' show the waves of ZnS:Cu, modulated to 100 c.p.s.

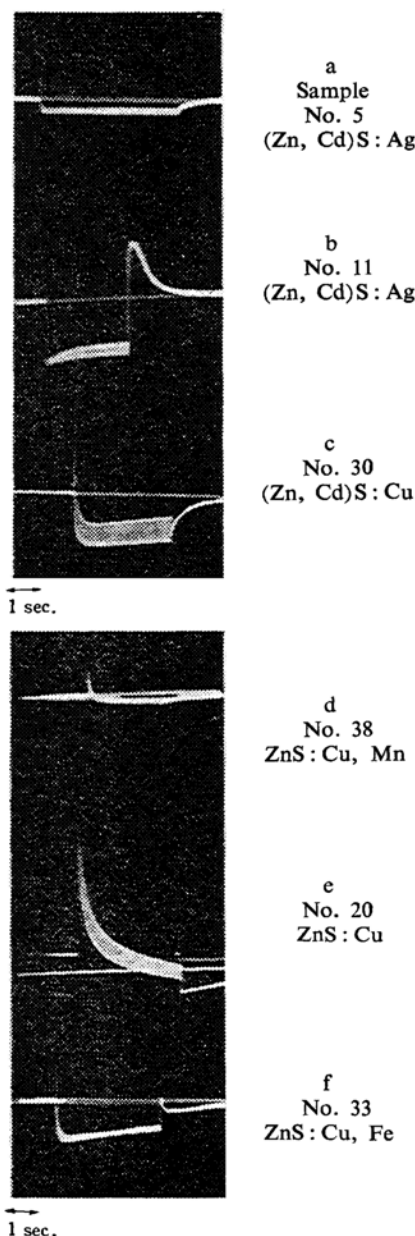


Fig. 3. Oscillogram of brightness at field application and removal. The luminescence of ultraviolet excited phosphors are affected by alternating electric field in following order, 1; steady luminescence, 2; field stimulation during excitation (the Gudden-Pohl effect), 3; field quenching during excitation, 4; cut-off stimulation or dip, 5; recovery.

stimulation only for ZnS:Cu, Fe, while (Zn, Cd)S:Ag (No. 11) and Zn(S, Se):Cu (No. 32) showed a different kind of cut-off stimulation from Matossi's, and had no sharp peak, but the emission increased gradually with time, reaching a maximum at about one second

after removal of the electric field, then decreased slowly to initial brightness. The increased emission at field removal was observed by the naked eye for the (Zn, Cd)S:Ag (No. 11). Their characteristics are shown in Fig. 3b. In Fig. 3 various typical brightness curves of luminescence which are influenced by the electric field are shown. In these figures the coordinate is brightness and the abscissa is time. Steady emission before the application of the electric field, momentary stimulation, field quenching, cut-off stimulation, and recovery are shown from left to right. During this period the phosphor was illuminated continuously by ultraviolet light.

The intensity of first stimulation depends on exciting ultraviolet intensity, the time interval between repeated field applications after first application and so on. The stimulated emission increased with the intensity of excitation and the time interval, and showed saturation. Fig. 4 shows stimulated emission as a function of the time interval at various exciting intensities.

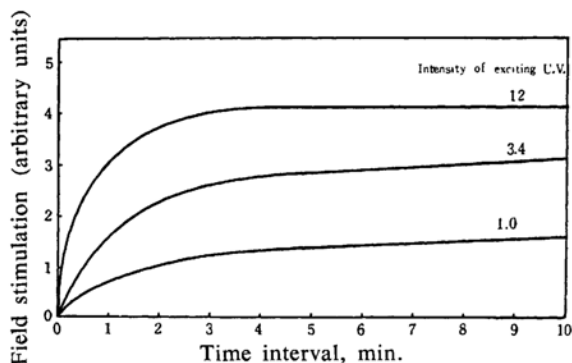


Fig. 4. Momentary field stimulation during excitation as a function of excited time interval at various intensity of ultraviolet. Phosphor ZnS:Cu (No. 17).

The time of application was about 10 sec. and in that time the momentary stimulation was over.

For the Gudden-Pohl effect after removal of the ultraviolet radiation the form of brightness pulse and dependence on kinds of activator and chemical composition of phosphors are similar to the first momentary stimulation during excitation.

The behavior under electric field, phosphorescence and infrared stimulation are shown in Table I. From this table, it is possible to compare the influence of electric field on the different phosphors. This is summarized as follows:

1. Many of the ZnS:Ag and (Zn, Cd)S:Ag phosphors with short persistent afterglow show appreciable field quenching during excitation, estimated to be 40% at a field intensity

of 10000 volts per cm., and have slight momentary stimulation. (Zn, Cd)S:Ag phosphors with longer afterglow show large momentary stimulation, but the quenching ratio does not decrease.

2. ZnS:Mn and (Zn, Cd)S:Mn which show considerable infrared stimulation have no field quenching, while ZnS:Mn which incorporates ZnO and also shows short afterglow and no infrared stimulation has a momentary stimulation whose duration is very short.

3. Cub.-ZnS:Pb with a short persistent phosphorescence and some infrared stimulation shows a strong field stimulation and a small field quenching, while hex.-ZnS:Pb with a long persistence and a strong infrared stimulation shows feeble field stimulation and no field quenching. ZnS:Cu, Pb (Fonda's phosphor) has a most remarkable infrared stimulation but shows feeble field stimulation and no field quenching.

4. The field sensitivity of ZnS:Cu and ZnS:Ag phosphors decreases by substitution of a large amount of cadmium for zinc, for example, (Zn_{0.20}, Cd_{0.80})S:Ag (red) and (Zn_{0.50}, Cd_{0.50})S:Cu (red) have no field stimulation and also no field quenching. But zinc-cadmium sulfide phosphors with medium substitution of cadmium for zinc still have considerable field sensitivity.

5. The influence on ZnS:Cu phosphors is very complicated. The zinc sulfide fired at 1020°C or higher is expected to have hexagonal structure, while sulfide fired below 1020°C is expected to have cubic structure. In this observation, the sulfide was fired at 1200°C for the hexagonal phosphor, and at 900°C for the cubic.

Their phosphorescence, infrared stimulation, and momentary stimulation during decay at field application are shown in Fig. 5 as a function of copper concentration. In this figure, the phosphorescence is plotted as an afterglow intensity after a lapse of one minute from removal of ultraviolet excitation, and the infrared stimulation as an initial flash-up intensity under infrared illumination also after one minute's decay, and the integral of light flash at field application (the area under the curve obtained in Fig. 6, in which the abscissa is time and the ordinate is the photocurrent from the photomultiplier) was taken as the measure of the Gudden-Pohl effect.

In hex.-ZnS:Cu, the phosphorescence is found to be increased by increasing the copper content and to reach a maximum at copper content of 3×10^{-5} mol. per one mol. of ZnS, and Gudden-Pohl stimulation is also increased by increasing the copper content and reaches a maximum at a copper content of 10^{-5} mol.

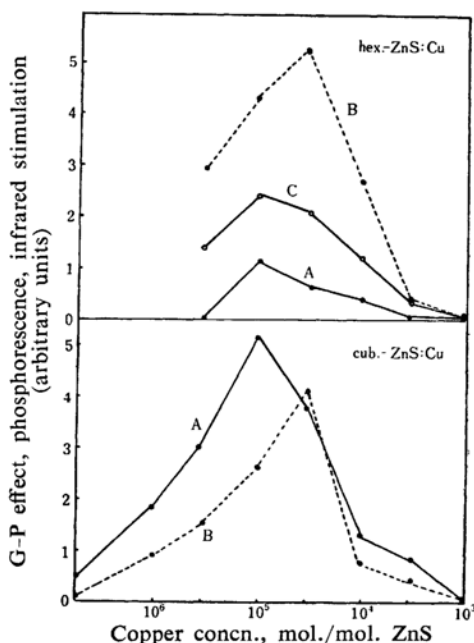


Fig. 5. The Gudden-Pohl effect during decay, phosphorescence and infrared stimulation as a function of copper concentration in hex. and cub. zinc sulfide phosphors. A. The Gudden-Pohl effect, B. phosphorescence, C. infrared stimulation.

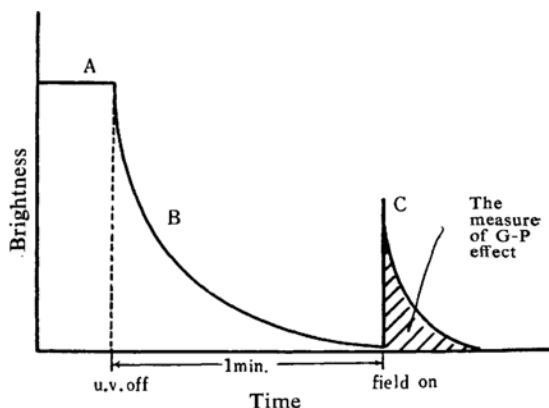


Fig. 6. The Gudden-Pohl effect (C) after removal of ultraviolet excitation. A: steady state luminescence, B: decay.

The zinc sulfide with 3×10^{-5} mol. copper has a very long persistent phosphorescence and the strongest infrared stimulation among the zinc sulfide phosphors activated with copper, but it shows weak field stimulation. Independent of the copper content the momentary field stimulation of hex.-ZnS:Cu is weaker than that of cub.-ZnS:Cu. The field stimulation of cub.-ZnS:Cu phosphors as a function of copper concentration is similar to that of hexagonal phosphors, but infrared stimulation is so feeble

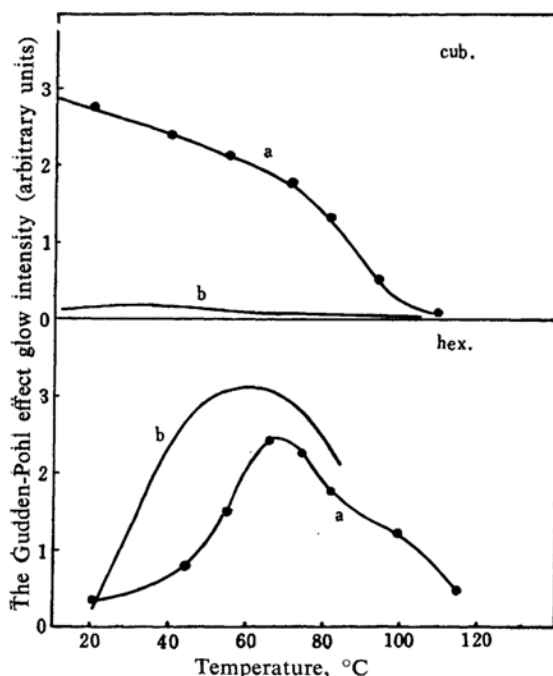


Fig. 7. The Gudden-Pohl stimulation as a function of temperature and glow curve. a: the Gudden-Pohl effect, b: glow intensity. Sample, cub.---ZnS:Cu (No. 16), hex.---ZnS:Cu (No. 24).

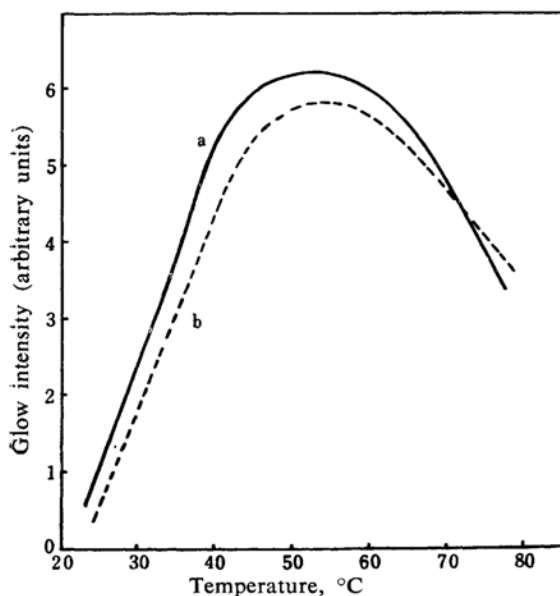


Fig. 8. Glow curves depending upon whether an electric field has been previously applied or not. Sample ZnS:Cu (No. 24). a: previously applied, b: not applied.

that it can not be detected. The Gudden-Pohl effect of cub.-ZnS:Cu with a suitable amount of copper is strong and shows relatively long duration, and it takes about one second to fall from flash-up to quenching level, and also several seconds to recover to initial brightness.

The intensity and decay of the flash by the electric field depend on temperature, that is, at higher temperature momentary stimulation at field application is sharper and its decay is more rapid. In Fig. 7 field stimulation is plotted as a function of temperature, and glow curves of phosphors which were excited and caused to decay at room temperature are shown in the same figure. The heating rate of glow curves was 0.2°C per second. In cub.-ZnS:Cu, the higher the temperature is, the smaller is the field stimulation between 20° and 120°C , and there is no peak in this temperature range. The momentary stimulation of hex.-ZnS:Cu increases with temperature reaching a maximum at 70°C , while the glow curve has a peak at 55°C .

Some knowledge of traps has been obtained from glow curve measurements by Bube⁶⁾. He proposed that a large number of traps are present in self-activated ZnS phosphors with no added copper impurity. The incorporation of copper up to 1.7×10^{-4} mol. (0.01%) causes the appearance of traps which are deeper than those present before the addition of copper. Incorporation of copper in amounts of more than 1.7×10^{-4} mol. causes disappearance of the deep traps due to copper.

Comparing our experimental results with the knowledge about traps, it could be considered that there is a maximum of momentary stimulation as a function of copper concentration at 10^{-5} mol. copper content and the number of deeper traps has a maximum value at 1.7×10^{-4} mol. copper content, that is, two maxima are uncoincident. So the deeper traps might not be contributing to the momentary stimulation.

Two glow curves of hex.-ZnS:Cu (24) depending upon whether or not the electric field has been previously are shown in Fig. 8. The application of the field was done after removal of excitation, and the time of application was ten seconds. A similar experiment was carried out by Destriau⁵⁾. In our observation, it can be seen that the maxima of two glow curves have about the same height. From this observation, we might assume that the deeper trap which corresponds to the glow peak at 55°C does not contribute to momentary stimulation at room temperature. Rather the increase of momentary stimulation at higher temperature may be ascribed to the effect of emptying the deeper

6) R. H. Bube, *Phys. Rev.*, **80**, 655 (1950).

traps which can release their electron thermally at higher temperature.

Summary

The effects of the electric field on the luminescence of ultra-violet excited zinc sulfide phosphors are shown as a function of kinds of activator and chemical composition of matrix. All phosphors were measured in an electroluminescent cell of common construction. The electric field was obtained from 50 c.p.s. alternating line. The Gudden-Pohl effect of both hexagonal and cubic ZnS:Cu increased with increasing copper content and reached a maximum at a content of 10^{-5} mol. The effect of cubic ZnS:Cu (10^{-5}) is the strongest in the zinc sulfide phosphors at room temperature.

Cubic sulfide phosphors activated by copper are sensitive to both momentary stimulation and field quenching.

Further, a relation between electron traps and the Gudden-Pohl effect was studied. From the temperature dependence of the Gudden-Pohl effect and glow curves, it might be assumed that the deeper trap which corresponds to a glow peak at 55°C does not produce the Gudden-Pohl effect at room temperature, rather the increase of the effect at higher temperature may be ascribed to the emptying of the deeper traps which can release their electrons thermally at higher temperature.

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